Task ID: 425.017
Task Title: Environmentally Benign Vapor Phase and Supercritical $CO_2$ Processes for Patterned Low k Dielectrics
Deliverable: Report on the demonstration of direct deposition of patterned organosilicate low k dielectric layers by photoinitiated CVD

Summary Abstract:
Selective deposition of patterned low k dielectric layers is an off roadmap, ESH focused approach to process step reduction during integrated circuit fabrication, the successful implementation of which would represent a substantial environmental and economic "win-win". Our long-range objective is to develop new methods to deposit, pattern and process low k materials to meet the roadmap goal of dielectric constants lower than 2.0. Photoinitiated CVD (piCVD), an evolutionary approach to assembly of low k materials, is being investigated for process simplification potential both during initial initiator pattern deposition and then during growth of low k material on those patterns. Photoinitiated CVD is an evolutionary approach to plasma enhanced CVD, with the main difference being that UV photons, rather than an electric field, are used to excite the reactive processes. Indeed, the use of light exposure in semiconductor manufacture is well known from rapid thermal processing technology.

Technical Results and Data:
Photoinitiated CVD was used to grow the low k material by initiating free radical chemistry from the patterned surface (Fig. 1). Selectivity is obtained by first patterning a thin base layer of a material containing abstractable hydrogens onto an aprotic base layer. Next a vapor phase initiator in the presence of ultraviolet light is used to generate growth sites for the low k material. Low k matrix precursors are subsequently assembles onto the reactive surface sites. The low k precursors include CVD capable silicate species which form molecular glasses.

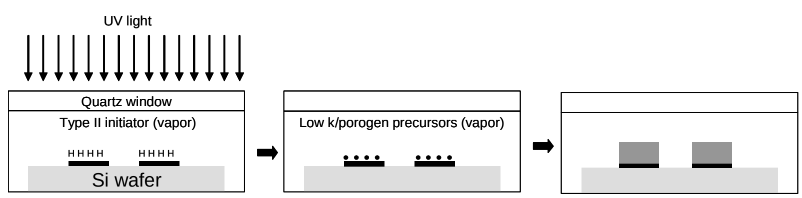
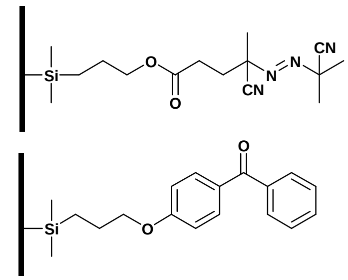



**Figure 1**. Schematic (not to scale) of piCVD process for selective deposition of patterned low k dielectric lines (dark grey, right) using existing 200 mm diameter chamber at MIT.

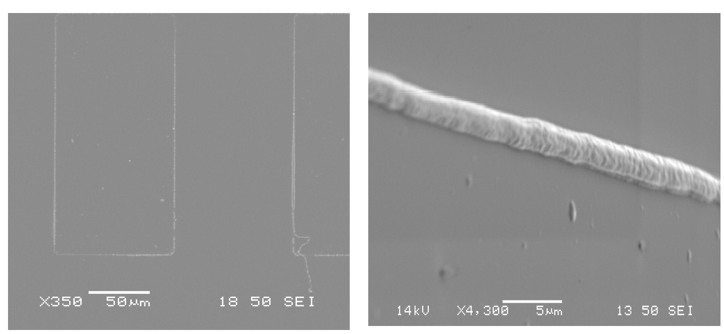
Tethered initiators have been prepared in order to grow low-k films directly from a substrate. Both a type I and type II initiators have been synthesized and tethered to a silicon wafer for preliminary experiments (Fig. 2). The optimal strategy for patterning the surface tethered initiators is currently being explored. Ideally, these initiators can be vapor deposited in a patterned way using a shadow mask. They can also be initiated in a patterned way using masked UV exposure. This dual strategy allows for flexibility in patterning in growth techniques.

Fig. 2. Type I and type II tethered radical initiators synthesized and attached to a silicon wafer.



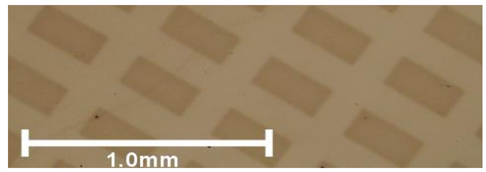

Direct deposition of patterned features by vapor deposition by using prepatterned, yet untethered, initiators was also successfully achieved. These selective piCVD experiments were performed utilizing microcontact printing of patterned type II initiator on silicon wafers. Initial pattern features were 100 μm by 200 μm rectangles and the benzophenone initiator was stamped from an acetone solution. Following stamping, wafer samples were exposed to 254 nm UV irradiation in the presence of vinyl deposition precursors. These conditions did not yield continuous deposition within the feature area but instead left thin (~3 μm) lines of deposition demarking the outside edge of the pattern. However, these lines do not always follow the outline of the stamp (Fig. 3). The high solubility of the initiator in the solvent was the likely cause of this phenomena, allowing for movement and concentration of the initiator during the drying of the solvent on the surface of the microcontact stamp.

Fig. 3. Scanning electron micrographs of 'outline' deposition created by first patterning experiments showing fidelity for one rectangle while the corner of an adjacent rectangle is not faithfully reproduced. Linewidth of the directly deposited feature is ~3 μm.



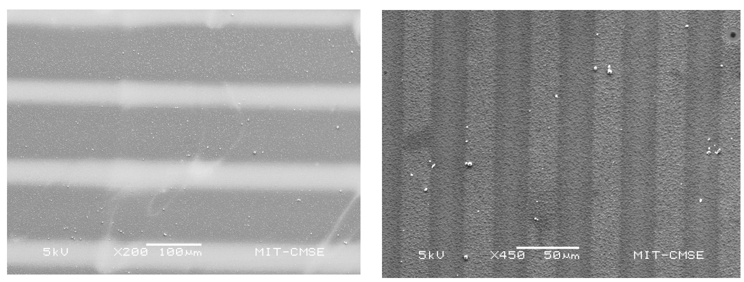
In order to avoid this issue, another type II initiator with significantly reduced solubility was selected, Michler's Ketone (MK). At first, use of the MK initiator yielded no deposited material. The affinity of the initiating species for the surface of the stamp over the surface of the wafer was determined to be the cause. To overcome this issue, the wafer surface was modified with a monolayer of a hydrophobic silane. This created a favorable change in surface energy of the wafer, allowing the deposition of completely filled in 100 µm scale rectangular features (Fig. 4).

Fig. 4. Optical micrograph of completely filled 100 x 200 µm rectangular features selectively deposited by piCVD.




Optimization of process conditions was required in order to create thicker features as initial 100 µm feature deposition only reached a total thickness of 30-50 nm. Deposition pressure and wavelength of UV excitation were both optimized, with a final wavelength of 365 nm irradiation selected. This allowed for higher deposition rates, increasing from 50 nm in 45 min to rates as high as 7.5 nm/min for deposition of 100 µm lines (Fig. 5, left).

Fig. 5. Scanning electron micrograph of lines and spaces at 100 µm (left) and 25 µm (right) resolution created through selective piCVD starting from a patterned of surface initiator. Feature heights are ~300 nm as determined by profilometry.




Using these improved conditions, smaller Line features in the 10-25 µm range were deposited with good repeatability (Fig. 5, right). Further optimization of feature size will be sought through modification of the surface patterning method. Other lithographic methods such as photo-bleaching of blanket initiator films will be undertaken.